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Positron Lifetime Spectroscopy for Investigation of Thin Polymer Coatings

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Abstract

In the aerospace industry, applications for polymer coatings are increasing. They are now used for thermal control on aerospace structures and for protective insulating layers on optical and microelectronic components. However, the effectiveness of polymer coatings depends strongly on their microstructure and adhesion to the substrates. Currently, no technique exists to adequately monitor the quality of these coatings. We have adapted positron lifetime spectroscopy to investigate the quality of thin coatings. Results of measurements on thin (25-μm) polyurethane coatings on aluminum and steel substrates have been compared with measurements on thicker (0.2-cm) self-standing polyurethane discs. In all cases, we find positron lifetime groups centered around 560 psec, which corresponds to the presence of 0.9-$Å^3$ free-volume cells. However, the number of these free-volume cells in thin coatings is larger than in thick discs. This suggests that some of these cells may be located in the interfacial regions between the coatings and the substrates. These results and their structural implications are discussed in this report.

Introduction

Thin polymer films are used extensively in electro-optical, pharmaceutical, aerospace, construction, and transportation industries. These polymers can be used as thin films and membranes or as thin coatings on appropriate substrates. In both cases, their effectiveness strongly depends on their molecular architecture. In the case of self-standing films, molecular architecture can involve the film's crystalline structure as well as its microvoid distribution function. In the case of coatings, greater emphasis is placed on the investigation of the bond between the coating and the substrate. Thus, a sensitive, nonintrusive technique is needed to investigate the morphological properties of thin films and thin coatings. We have developed a low-energy positron flux generator ideally suited for such studies. (See refs. 1 and 2.) This generator has been used to investigate free-volume characteristics of polyurethane coatings on aluminum and steel substrates. The results of this investigation are discussed in the following sections of this report.

Experimental Procedure

A slow positron flux generator has been developed for microstructural characterization of thin polymer films and coatings. Figure 1 shows the generator assembly used for measuring free-volume characteristics in thin self-standing films. Figure 2 shows a modified version of the positron generator used for investigation of thin polymer coatings on metal substrates and their bond integrity. In both these applications, the main objective is to measure the positron lifetime spectrum in the film or coating *without* any interference from the moderator or substrate strips, respectively. A brief description of this measurement technique for thin film coatings follows.

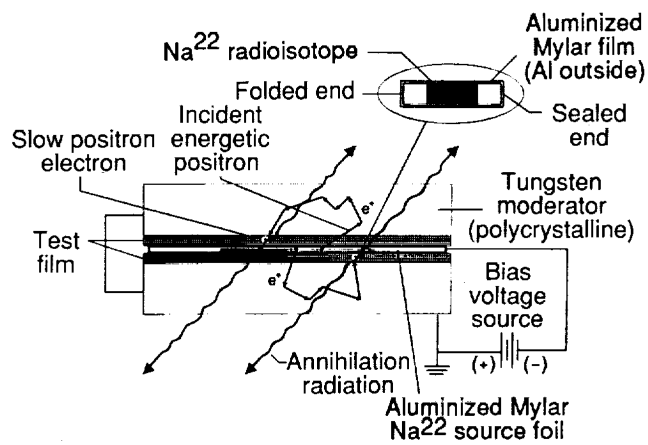


Figure 1. Low-energy positron flux generator assembly.

A 200-μC Na^{22} source deposited on a 2.5-μm-thick aluminized Du Pont Mylar film is sandwiched between two 2.54-cm by 2.54-cm tungsten strips that are 0.0127 cm thick. Two 2.54-cm by 2.54-cm polyurethane film coatings on metallic substrates insulate the tungsten moderator strips from the aluminized Mylar source holder. The aluminized side of the source foil is in contact with the metallic substrate on which the polyurethane coating is applied. A potential difference of ± 60 V is applied between the tungsten strips and the aluminized source foil. Thermalized positrons diffusing out of the moderator

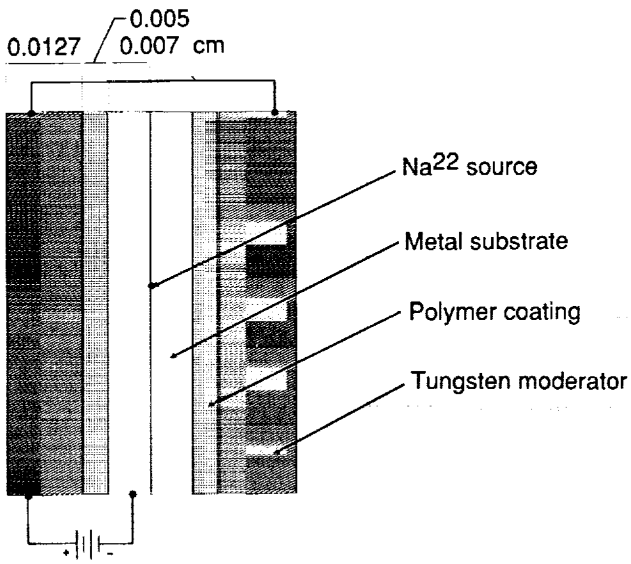


Figure 2. Slow positron beam generator.

strips are attracted to the metallic substrates when they are at a negative potential. These positrons have to drift through the polyurethane coatings to reach the metallic substrates. They will, in all likelihood, annihilate in the polyurethane coatings before reaching the substrates. On the other hand, the positrons diffusing out of the moderator strips are forced back into the strips when the substrates are at a positive potential. Thus, more positrons annihilate in the tungsten moderator strips when the coating substrates are positive than when they are negative.

Careful measurements with well-characterized Du Pont Teflon films have shown that the excess of positrons stopping in the moderator strips when the coating backings are at a positive potential is 4 percent. (See refs. 1 and 3.) Thus, subtraction of 96 percent of the positive substrate bias lifetime spectrum from the negative substrate bias lifetime spectrum should give the lifetime spectrum exclusively due to the positrons annihilating in the polyurethane coatings.

The lifetime spectra were acquired by using a standard fast-fast coincidence counting system with a resolution of 250 psec. These lifetime spectra were then analyzed by standard deconvolution techniques. Lifetimes in excess of 500 psec are assumed to be associated with orthopositronium (O-psec) annihilations. With the previously established relationship between O-psec lifetime and free-volume cell radius (refs. 4 and 5), the average volumes of the cells can be readily calculated.

Experimental Results

To assess the quality of thin polyurethane film coatings, we decided to first measure the lifetime spectrum in a thick polyurethane disc. Any deviation from the thick disc spectrum was interpreted as an indication of defects (microvoids) in the thin films or film-substrate interfacial regions. Figure 3 shows a typical positron lifetime spectrum in a 0.254-cm-thick polyurethane disc. This spectrum was analyzed by using the POSFIT-EXTENDED program (ref. 6). A two-component analysis gave the best least squares fit to the data, and table I summarizes the results.

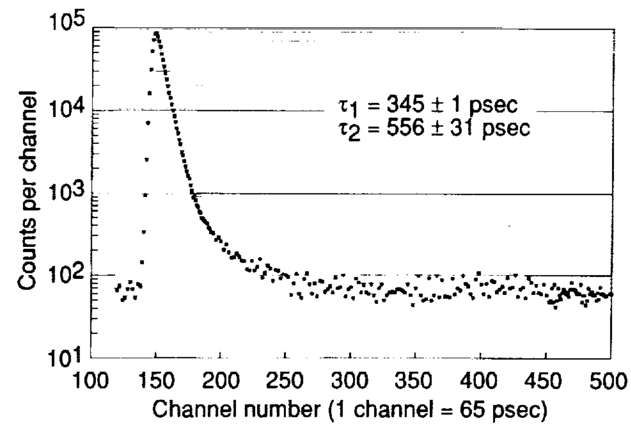
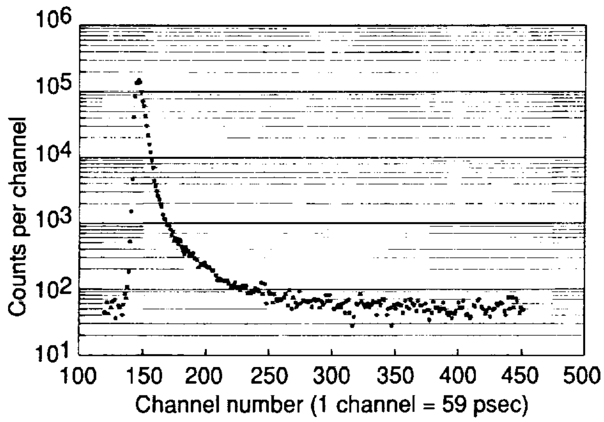


Figure 3. Typical positron lifetime spectrum in thick polyurethane disc.

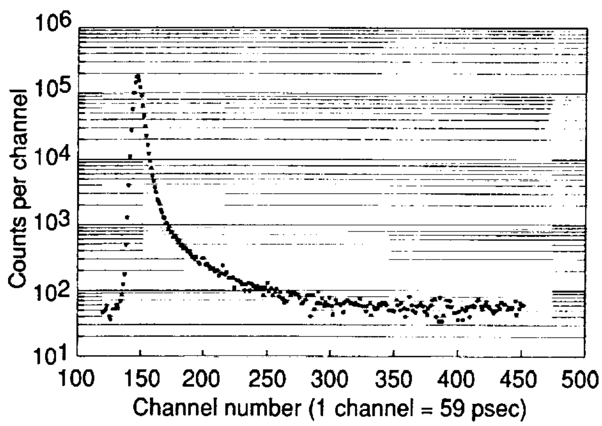
Table I. Summary of Positron Lifetime Values in Thick Polyurethane Disc and Transparent Polyurethane Coatings

Test sample	Lifetime, τ_1, psec	Intensity, I_1, percent	Lifetime, τ_2, psec	Intensity, I_2, percent
Thick polyurethane disc	345 ± 1	85 ± 1	556 ± 31	15 ± 1
Polyurethane coating on steel	192 ± 4	74 ± 1	572 ± 35	26 ± 1
Polyurethane coating on aluminum	231 ± 4	74 ± 1	562 ± 35	26 ± 1

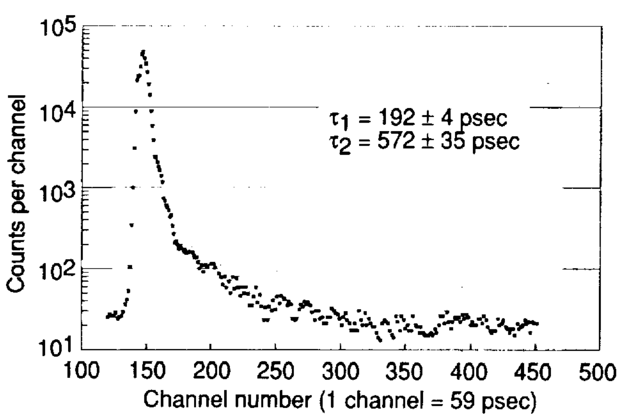
Polyurethane coatings on aluminum and steel substrates were analyzed with the slow positron flux generator shown in figure 2. The efficiency of the generators shown in figures 1 and 2 is 4 percent (refs. 1 and 2). Figure 4 illustrates typical positron lifetime results in polyurethane coatings. Figures 4(a)



(a) Source bias = −60 V.



(b) Source bias = +60 V.



(c) Difference spectrum.

Figure 4. Typical positron lifetime spectrum in coated steel.

and 4(b) show the spectra observed with ∓60-V bias, respectively, on the source foil. Figure 4(c) shows the difference between the −60-V bias spectrum and 96 percent of the +60-V bias spectrum. This *difference spectrum* represents the true positron lifetime spectrum in the coatings and the coating-steel interfacial region. Once again, a two-component analysis gave the best least squares fit to the data. Lifetime results in coatings on aluminum and steel substrates are included in table I for comparison.

Discussion

From the data summarized in table I, the following differences between the lifetime spectra of the disc and the coatings are noted:

1. The lifetime of the shorter-lived component (τ_1) is longer in the thick disc than in the thin coatings.
2. The intensity (I_2) of the longer life component (τ_2) is higher in the thin coatings than in the thick disc.

The first difference implies that the morphologies of the thin polyurethane coatings slightly differ from that of the thick polyurethane disc. However, the second difference implies that more microvoids are present in the thin film coatings than in the thick disc. Some of these microvoids may be located in the interfacial regions of the coating-substrate bonds. However, their volume is only ≈0.9 Å^3, which is too small to significantly impact the coating bond strength. Microvoids of ≥ 2 Å^3 are needed to significantly impact the bond strength.

Lifetime measurements were also made in polyurethane coatings of a different variety on steel substrates. These polyurethane coatings were translucent, whereas the coatings used in the previous samples (table I) were transparent. Table II summarizes the results for the translucent coatings. Note, the microstructures of the two types of polyurethane coatings on steel substrates are almost identical. The intensity of the longer life component in translucent coatings is slightly larger than it is in the transparent coatings. This difference is more indicative of differences in the morphologies of the two types of polyurethanes than the quality of coatings-substrate bond.

Table II. Summary of Positron Lifetime Values in Thin Translucent Polyurethane Film Coatings

Test sample	Lifetime, τ_1, psec	Intensity, I_1, percent	Lifetime, τ_2, psec	Intensity, I_2, percent
Polyurethane coating on steel	168 ± 1	70 ± 1	570 ± 31	30 ± 1

Concluding Remarks

A slow positron flux generator has been developed to monitor the quality of thin polymer coatings on metal substrates. This generator has been used to monitor the quality of coatings and their bonds to the substrates for a number of polyurethane coatings on aluminum and steel substrates. A comparison of positron lifetimes in thin coatings with those observed in thick polyurethane discs indicates that their morphologies are rather different. Additionally, the presence of more 0.9-$Å^3$ free-volume cells (microvoids) in thin film coatings than in thick discs suggests that some of these microvoids may be located in the interfacial regions of the coatings. Even though these results do not necessarily mean that the coatings or their bonds to the substrates are of good quality, they do demonstrate that positron lifetime spectroscopy can provide very useful information about the quality of the coatings and their adherence to the substrates.

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December 7, 1992

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13. ABSTRACT *(Maximum 200 words)*
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